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Report Title

Final Report on A Predictive Multiscale Model of Wear

ABSTRACT

This report describes the development of an ab initio version of density functional theory + U (DFT+U) theory that then permitted high quality quantum mechanics simulations of the tensile and shear properties of chromium and iron oxides. A multiscale model that had been devised earlier by the PI for describing tensile load response was extended to study shear deformation across scales. Analysis of atomic scale deformations provided insight into the mechanical properties (e.g., tensile and shear strengths and moduli)calculated. The oxides were shown to yield more easily via shearing than via tensile displacements, which can be understood by the reduced loss of metal-oxygen bonds during shear. The relative ease of shearing has implications for the oxides forming in gun tubes, namely that despite their brittle nature, the shear forces exerted by the propellant gases and projectile are largely responsible for wear in gun tubes.

List of papers submitted or published that acknowledge ARO support during this reporting period. List the papers, including journal references, in the following categories:

(a) Papers published in peer-reviewed journals (N/A for none)

N. J. Mosey and E. A. Carter, "Ab initio Evaluation of Coulomb and Exchange Parameters for DFT+U Calculations," Phys. Rev. B, 76, 155123 (2007).

N. J. Mosey, P. Liao, and E. A. Carter, "Rotationally-Invariant ab initio Evaluation of Coulomb and Exchange Parameters for DFT + U Calculations," J. Chem. Phys., 129, 014103 (2008).

E. A. Carter, "Challenges in Modeling Materials Properties without Experimental Input," Science, 321, 800 (2008).

N. J. Mosey and E. A. Carter, "Ab initio LDA+U Prediction of the Tensile Properties of Chromia across Multiple Length Scales," J. Mech. Phys. Solids, 57, 287 (2009).

N. J. Mosey and E. A. Carter, "Shear Strength of Chromia across Multiple Length Scales from First Principles," Acta Materialia, 57, 2933 (2009).

P. Liao and E. A. Carter, "Ab initio DFT+U predictions of tensile properties of iron oxides," J. Mater. Chem., 20, 6703 (2010).

P. Liao and E. A. Carter, "Ab initio DFT+U predictions of the shear response of iron oxides," Acta Materialia, 58, 5912 (2010).

Number of Papers published in peer-reviewed journals: 7.00

(b) Papers published in non-peer-reviewed journals or in conference proceedings (N/A for none)

Number of Papers published in non peer-reviewed journals: 0.00

(c) Presentations

Invited Talks Given by PI:

December 2, 2010 “Chemistry and Mechanics of Steel Erosion from First Principles Simulations,” at the 2010 Materials Research Society Fall Meeting, Boston, MA.

October 15, 2009 “Quantum-Based Descriptions of Materials Behavior,” at the NRC Solid State Sciences Committee Fall Meeting, Irvine, CA.

September 16, 2009 “Ab Initio Treatment of Excited States and Strongly Correlated Electrons in Crystals,” Plenary Lecture at the 2009 ETSF Workshop on Electronic Excitations, Evora, Portugal.

May 25, 2009 “Status and Challenges in Modeling Molecules and Materials for Energy Conversion Technologies,” at the 215th Electrochemical Society Meeting, San Francisco, CA.

March 19, 2009 “Design of Robust Protective Coatings for Metal Components Subjected to Extreme Conditions,” at the Computer Aided Molecular Design Conference, St. Johns, Antigua.

December 3, 2008 “First Principles Design of Metal Alloys and Oxides to Limit Chemical Degradation and Creep,” at the 2008 Materials Research Society Fall Meeting, Boston, MA.

September 25, 2008 “Quantum Mechanics Methods and Applications for Predicting Behavior of Materials,” at the 44th Symposium on Theoretical Chemistry, Ramsau am Dachstein, Austria.

September 5, 2008 – “Quantum-based multiphysics and multiscale descriptions of materials behavior,” plenary lecture at the Conference on Computational Physics 2007, Brussels, Belgium.

August 19, 2008 – “Understanding the Behavior of Metal Oxides,” at the 236th American Chemical Society National Meeting and Exposition, Philadelphia, PA.

March 26, 2008 – “Bob Shaw: Program Manager (& Person) Extraordinaire,” at the Robert Shaw Colloquium, Army Research Laboratory, Aberdeen, MD.

November 2, 2007 – “Status and Challenges in Quantum Mechanics Based Simulations of Materials Behavior,” at the NSF World Technology Evaluation Center US Baseline Workshop on Simulation Based Engineering and Science, Arlington, VA.

October 9, 2007 – “Predictive modeling of materials at the nanoscale: What can we learn from quantum mechanics?” at the NSF Workshop on Predictive Modeling of Materials at the Nanoscale, Washington, DC.

August 21, 2007 – “Quantum-based Simulations of the response of materials to extreme conditions,” at the 234th American Chemical Society National Meeting, Boston, MA.

June 14, 2007 – “What to do when Density Functional Theory Fails? Beyond DFT to Improved Descriptions of Materials Behavior,” at the Mainz Materials Simulation Days, 2007, Mainz, Germany.

March 25, 2007 – “Accuracy and validity of first-principles based simulations of material behavior, in the Symposium for Measures of Accuracy and Reliability in Molecular Simulation,” at the 23rd American Chemical Society National Meeting, Chicago, IL.

Contributed Talks:

September 9, 2008 – “Ab Initio Evaluation of Coulomb and Exchange Parameters for DFT+U Theory: Application to Transition Metal Oxides,” poster at PRISM’s Fall Open House, Princeton University, Princeton, NJ. (presented by Peilin Liao)

August 21, 2008 – “Ab Initio Evaluation of Coulomb and Exchange Parameters for DFT+U Theory: Application to Transition Metal Oxides,” talk at the 236th ACS National Meeting and Exposition, Philadelphia, PA. (presented by Peilin Liao)

July 20, 2008 – “Ab Initio Evaluation of Coulomb and Exchange Parameters for DFT+U Theory: Application to Transition Metal Oxides,”

poster at the American Conference on Theoretical Chemistry, Northwestern University, Evanston, IL. (presented by Peilin Liao)

March 17, 2008 – “Quantum-Based Theories for Molecules and Materials in the Carter Group,” poster at the PRISM/PCCM/MIRTHE/CNSA University-Industry Research Symposium, Princeton University, Princeton, NJ. (presented by Peilin Liao)

November 17, 2007 - “First-Principles calculation of iron oxides – towards understanding of steel corrosion,” poster at the Princeton Research Symposium 2007 at Princeton University, Princeton, NJ. (presented by Peilin Liao)

May 28, 2007 – “Development of First-Principles Cohesive Laws for Strongly-Correlated Materials,” talk at the Canadian Society for Chemistry Conference and Exhibition, Winnipeg, Manitoba. (presented by Nicholas Mosey)

Number of Presentations: 21.00

Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts): 0

Peer-Reviewed Conference Proceeding publications (other than abstracts):

Number of Peer-Reviewed Conference Proceeding publications (other than abstracts): 0

(d) Manuscripts

Number of Manuscripts: 0.00

Patents Submitted

Patents Awarded

Awards

2010 - Molecular Foundry Distinguished Lecturer, Lawrence Berkeley National Laboratory
Coover Lecturer in Chemistry, Iowa State University

Material Simulation Distinguished Lecturer, Penn State University
Pelz Memorial Lecturer in Mechanical and Aerospace Engineering, Rutgers University
Noyes Lecturer in Physical Chemistry, University of Texas, Austin

2009 - Member, International Academy of Quantum Molecular Science

2008 - Member, National Academy of Sciences
Fellow, American Academy of Arts & Sciences
EaSTChem Visiting Fellow, Universities of Edinburgh and St. Andrews, Scotland
Welch Distinguished Lecturer
Coulson Lecturer, University of Georgia
Kivelson Lecturer, University of California, Los Angeles

2007 - American Chemical Society Award for Computers in Chemical and Pharmaceutical Research

Graduate Students

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
Peilin Liao	1.00
Philip Casey	0.25
Donald Johnson	0.25
FTE Equivalent:	1.50
Total Number:	3

Names of Post Doctorates

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
Nicholas Mosey	0.42
FTE Equivalent:	0.42
Total Number:	1

Names of Faculty Supported

<u>NAME</u>	<u>PERCENT SUPPORTED</u>	National Academy Member
Emily A. Carter	0.17	Yes
FTE Equivalent:	0.17	
Total Number:	1	

Names of Under Graduate students supported

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
FTE Equivalent:	
Total Number:	

Student Metrics

This section only applies to graduating undergraduates supported by this agreement in this reporting period

The number of undergraduates funded by this agreement who graduated during this period: 0.00

The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields:..... 0.00

The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields:..... 0.00

Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale):..... 0.00

Number of graduating undergraduates funded by a DoD funded Center of Excellence grant for Education, Research and Engineering:..... 0.00

The number of undergraduates funded by your agreement who graduated during this period and intend to work for the Department of Defense 0.00

The number of undergraduates funded by your agreement who graduated during this period and will receive scholarships or fellowships for further studies in science, mathematics, engineering or technology fields:..... 0.00

Names of Personnel receiving masters degrees

NAME

Total Number:

Names of personnel receiving PHDs

NAME

Donald F. Johnson

Total Number:

1

Names of other research staff

NAME

PERCENT SUPPORTED

FTE Equivalent:

Total Number:

Sub Contractors (DD882)

Inventions (DD882)

Scientific Progress

see attachment

Technology Transfer

Scientific Accomplishments

This final report summarizes research accomplished during July 19, 2006 to July 31, 2010 on developing and applying first principles quantum mechanics methods to describe mechanical wear of chrome-plated steel gun tubes. During this grant, we published seven articles and gave 15 invited talks and 6 contributed presentations (talks and posters) at conferences under ARO-DRI sponsorship. To accurately calculate from first principles the mechanical properties of oxides that contribute to gun tube wear and erosion, the electronic structure of the material must be described properly. The first half of this grant was devoted to developing a quantum mechanics method that was both accurate for such materials and non-empirical so that it could be predictive. This entailed development of our *ab initio* DFT+U theory, published in *Physical Review B* and the *Journal of Chemical Physics*. We next published an Invited Perspective article in *Science* on the status and challenges in quantum mechanics based materials modeling, an article in the *Journal of Mechanics and Physics of Solids* that discusses the response of chromia to tensile loads across varying length scales, and an article in *Acta Materialia*, which derives a method for predicting shear strengths across multiple length scales and predicts the response of chromia to shear forces. In 2010, we published two papers that use the universal scaling laws we derived for tensile and shear deformations to compare the mechanical response of three iron oxides, Fe_2O_3 , FeO , and Fe_3O_4 , across a variety of length scales. All of these papers employed our *ab initio* DFT+U theory that provides the correct electronic structure for chromia and the iron oxides, producing accurate mechanical properties.

A. Ab Initio DFT +U Method

Transition metal oxides such as Cr_2O_3 , FeO , and Fe_2O_3 are examples of a larger class of materials known as strongly correlated electron materials (SCEMs), namely those for which a mean-field description of electron correlation - such as that provided in density functional theory (DFT) - completely fails. In conventional DFT calculations, a model is chosen for the electron exchange-correlation (XC) density functional, since the exact XC functional is unknown. By construction, the model necessarily approximates exchange interaction energies. In many cases, the typical approximations [the local density approximation (LDA) or the generalized gradient approximation (GGA)] work extremely well for a variety of ground state properties. However, there exist classes of materials and phenomena for which the LDA and GGA simply do not contain the correct physics. Here we are interested in one of these cases, namely the case in which the material has multiple open-shell valence electrons occupying tightly contracted orbitals. The open shell d-electrons of the transition metal ions are treated improperly by the LDA and the GGA, because their approximate intra-atomic exchange energies do not exactly cancel the spurious Coulomb repulsion of each open-shell d-electron with itself, leading to the so-called “self-interaction error (SIE)”. The consequences of the inexact cancellation by approximate DFT functionals are quite dire: not just quantitative but qualitative failure, with semiconductors sometimes predicted to be metals (e.g., NiO and FeO). Why does the electronic structure go so horribly wrong? To minimize this spurious net Coulomb repulsion, the open-shell electrons inappropriately delocalize, and delocalized electron distributions are metallic. So the physics is ruined by the SIE. Why is the failure so dramatic just in the cases enumerated? Because they each have large numbers of large intra-atomic exchange interactions, each of which is in error and the error is cumulative.

By contrast, this spurious self-Coulomb repulsion is exactly cancelled by the exact exchange energy in Hartree-Fock (HF) theory. Thus, a solution, as first articulated by Lichtenstein and coworkers,¹ comes in the form of treating the intra-atomic Coulomb and exchange interactions properly with HF theory, while treating the rest of the system with DFT. This is the essence of the DFT+U theory, which has been shown to provide accurate descriptions of the ground state electronic structure of SCEMs. Are there drawbacks of DFT+U theory? There are two: (i) a choice must be made for the choice of “U”, actually U-J, the difference between averaged intra-atomic Coulomb (U) and exchange (J) energies. The selection is usually empirical (based on comparison with experimental observables on known materials), which is problematic both formally and practically – what if one wants to study a brand new material for which no measurements have been made? Another approach involves constrained DFT calculations to determine U-J,² but this has the obvious drawback of establishing U-J from the very theory one is trying to correct. (ii) Once chosen, U-J is fixed for the material at hand. While this is sufficient in many instances, circumstances exist where a dynamical treatment of U-J is really needed. For example, metal-insulator transitions are not treated properly with DFT+U, since HF does not treat metals properly (generating spurious charge density waves, etc.).³ For such phenomena, use of the dynamical mean field theory (DMFT) is appropriate, but such phenomena are not of concern in the present work.

Our contribution to DFT+U theory addresses the first drawback. We developed a scheme to determine U - J fully non-empirically and without SIE from *ab initio* unrestricted Hartree-Fock (UHF) calculations on electrostatically embedded clusters. We derived a relationship between U and J and the Coulomb and exchange integrals evaluated using the full set of occupied UHF molecular orbitals (MOs) for the electrostatically embedded clusters. We evaluate U - J using increasingly larger clusters representing the crystal of interest, where the clusters are embedded in very large point charge arrays to represent the Madelung potential of the extended crystal. Cationic nearest neighbors to the anionic atoms on the surface of each cluster are not described as point charges, but instead are represented by effective core potentials, in order to account for core-valence electron Pauli repulsion between the valence electrons of the surface anions and the neighboring cation cores. The cluster size is increased until we reach converged values of U - J . The technique has been used to evaluate *ab initio* values of U and J for Cr_2O_3 , FeO , and Fe_2O_3 thus far. Unlike the empirically-derived values for these materials, the parameters we derive exhibit physically reasonable periodic trends. For example, the value of U - J for Cr^{3+} is smaller than the corresponding value for Fe^{3+} , which makes sense since Fe’s orbitals are more contracted than Cr’s due to Fe’s larger effective nuclear charge (Fe is less well screened than Cr). Secondly, the value of U - J for Fe^{2+} is smaller than for Fe^{3+} , which again makes sense since Fe^{3+} has more contracted orbitals than Fe^{2+} . By contrast, empirically derived values for U - J give exactly the opposite (unphysical) trends. DFT+U calculations using the *ab initio* parameters yield bulk electronic and structural ground state properties in good agreement with experiment. As such, this approach provides the means to perform accurate and fully-predictive DFT+U calculations of SCEMs. Two papers have appeared on this work: N. J. Mosey and E. A. Carter, “*Ab initio* Evaluation of Coulomb and Exchange Parameters for DFT+U Calculations,” *Phys. Rev. B*, **76**, 155123 (2007) and N. J. Mosey, P. Liao, and E. A. Carter, “Rotationally-Invariant *ab initio* Evaluation of Coulomb and Exchange Parameters for DFT + U Calculations,” *J. Chem. Phys.*, **129**, 014103 (2008).

B. Response of Cr₂O₃ to Tensile Loads

Chrome-plated gun tubes will have a layer of chromia (Cr₂O₃) on them upon exposure to moist air. Understanding the mechanical response of chromia will give some insight into wear properties of the gun tube. Hence, we first evaluated with our *ab initio* DFT+U theory various mechanical properties associated with the fracture of chromia by applying tensile loads along the [0001] and $[0\ 1\ \bar{1}\ (3/2)(a/c)^2\ 2]$ directions. Loading along these directions led to formation of the most stable surfaces and therefore we presume these directions to be the most likely to lead to fracture. Tests of this assumption provided justification for this selection of directions. The properties investigated included the tensile strength, elastic constants, and fracture energies. The tensile strengths were evaluated using an ideal tensile test, which provides the theoretical tensile strength, and by fitting the calculated data to universal binding energy relationships (UBERs), which permit the extrapolation of the calculated results to arbitrary length scales. The results demonstrate the ability of an UBER that accounts for fracture surface relaxation to yield a realistic estimate of the tensile strength of a 10 micron thick sample of Cr₂O₃ using data obtained through calculations on nanoscopic systems. We predict that Cr₂O₃ will fracture most easily in the $[0\ 1\ \bar{1}\ (3/2)(a/c)^2\ 2]$ direction, with a best estimate for the tensile strength of 386 MPa for a 10 micron grain, which is quite consistent with flexural strength measurements for chromia. The grain become considerably stronger at the nanoscale, where we predict a tensile strength along the same direction of 32.1 GPa for 1.45 nm crystallite. The results also provide insight into the origin of the direction dependence of the mechanical properties of Cr₂O₃, with the differences in the behavior along different directions being related to the number of Cr-O bonds supporting the applied tensile load. This work was published in *N. J. Mosey and E. A. Carter, "Ab initio LDA+U Prediction of the Tensile Properties of Chromia across Multiple Length Scales," J. Mech. Phys. Solids 57, 287 (2009).*

C. Shear Response of Chromia

We then applied the *ab initio* LDA + U (U-J=7.7 eV) to calculate shear strengths of chromia. First we needed to develop and test a renormalization scheme describing the behavior of materials subjected to shear up to the point at which slip occurs. The model we devised is analogous to the tensile-load UBER and leads to a size-dependent definition of the shear strength, τ_c . The quantities that enter into this definition can be derived directly from calculations on nanoscale samples, and thus this model provides a means of predicting τ_c at mesoscopic length scales from data obtained through atomistic calculations. The model was used to evaluate τ_c of chromia (Cr₂O₃) for three relevant slip systems. The *ab initio* LDA + U calculations clearly demonstrate the ability of the model to account for the size-dependence of τ_c of this material. For instance, the *ab initio* LDA + U calculations yield values of τ_c ranging from 19.4 to 29.4 GPa, depending upon the slip direction, slip plane, and level of theory, which is consistent with theoretical estimates of the ideal shear strength of the material. Meanwhile, values of τ_c between 189 to 342 MPa are obtained when the quantum mechanics data are used in conjunction with the proposed scheme to predict τ_c for a grain that is 10 microns thick. The direction and plane most likely to slip first is predicted to be $[12\bar{3}\bar{1}](01\bar{1}2)$. Although we were unable to find experimental data against which to compare the results, ceramics generally have shear strengths in the range of a few 100 MPa. This indicates that the rescaling and extrapolation

scheme employed here is suitable for estimating mesoscopic shear strengths. The development of this new universal scaling law for slip and its application to chromia was published in *N. J. Mosey and E. A. Carter, Acta Materialia*, **57**, 2933 (2009).

D. The PI was asked to write a Perspective article in *Science* for a special section on theoretical chemistry which appeared in August 2008. The article concerns challenges and frontiers in quantum mechanics based materials modeling. The paper offers a candid evaluation of methods ranging from the most accurate (quantum chemistry and quantum Monte Carlo) to the least expensive yet often accurate enough (density functional theory), including also theories for electronic excited states in condensed matter. The paper offers recommendations as to which methods should be used for various materials classes and phenomena. It points out pros and cons of each method, which methods should *not* be used or at least when one may get either the wrong answer or the right answer for the wrong reason. The article ends by discussing a variety of materials and phenomena that still pose great challenges in terms of accurate and efficient quantum based materials modeling, primarily due to the difficulty of integration of theories for complex materials. (*E. A. Carter, "Challenges in Modeling Materials Properties without Experimental Input," Science*, **321**, 800 (2008))

E. Mechanical Properties of Iron Oxides

Stress-corrosion cracking of steel is a ubiquitous phenomenon in which steel is chemically corroded, followed by mechanical failure induced by applied loads. The products of steel corrosion in moist air at high temperature (>570 °C) are Fe_2O_3 , FeO , and Fe_3O_4 . The oxidation states and coordination of Fe in these three types of iron oxides are different: Fe^{2+} and hexacoordinate for FeO , Fe^{3+} and hexacoordinate for Fe_2O_3 , mixed valence of Fe^{2+} and Fe^{3+} and a combination of hexacoordinate and tetra-coordinate for Fe_3O_4 . The crystal lattices also differ, as shown in Figure 1: FeO is a rock-salt crystal, Fe_2O_3 is a corundum-type crystal, and Fe_3O_4 has a spinel structure. Both electronic and geometric structural differences will contribute to trends in mechanical properties of the three oxides.

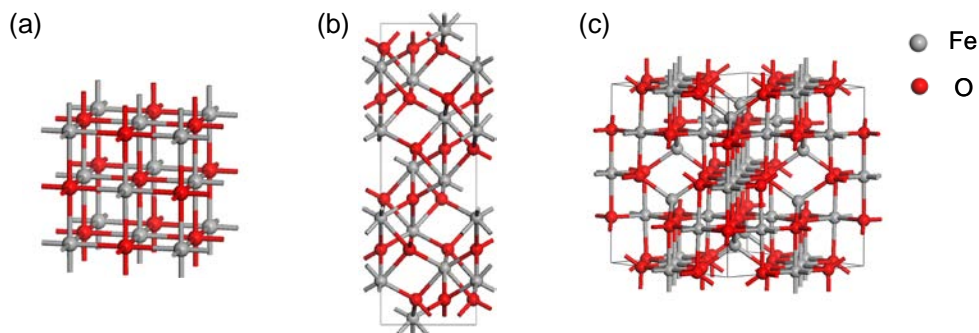


Figure 1. (a) FeO , (b) Fe_2O_3 , and (c) Fe_3O_4 .

We carried out a detailed study of the tensile and shear response of these three iron oxides using our ab initio DFT+U theory. The U-J parameters to be used in the DFT+U calculations for the iron oxides were evaluated in our earlier work (N. J. Mosey, P. Liao, and E. A. Carter, "Rotationally-Invariant ab initio Evaluation of Coulomb and Exchange Parameters for DFT + U Calculations," *J. Chem. Phys.*, **129**, 014103 (2008)). They are: 3.7 eV for FeO and 4.3 eV for Fe_2O_3 . For Fe_3O_4 , the previous unrestricted Hartree-Fock (UHF) theory scheme used for

evaluating U-J is not applicable because some of the Fe ions are of mixed valence character, meaning that one electron is delocalized over two Fe atoms. Since the UHF method derives a U-J assuming the electrons for which U-J are being derived are localized on one atom, we cannot apply it cases where the electrons spread out over more than one atom. Instead we use 4.3 eV for Fe^{3+} ions present in Fe_3O_4 (akin to the Fe^{3+} ions in Fe_2O_3) and using the average of the Fe^{2+} and Fe^{3+} values determined for FeO and Fe_2O_3 (4.0 eV) for the sites that have mixed +2 and +3 oxidation states in the crystal.

Our previously derived universal binding energy relationship for tensile loading was employed to extrapolate atomic scale ab initio DFT+U data to macroscopic sample sizes. The extrapolated macroscopic predictions are consistent with experimental measurements. The ordering of tensile strengths was found to be $\text{FeO} < \text{Fe}_3\text{O}_4 < \text{Fe}_2\text{O}_3$, which correlates with increasing ionicity (as given by the formal charge on the Fe cations) in the three oxides. The direction that has weakest tensile strength is predicted to be along $[011\ (3/2)(a/c)^22]$ for Fe_2O_3 and along $[001]$ for both FeO and Fe_3O_4 . The direction dependence of tensile properties for these three iron oxides can be understood via a local bond strain analysis. We also predicted that loading FeO along $[110]$ and Fe_3O_4 along $[001]$ or $[111]$ produces a plastic response prior to brittle fracture at high temperature. This work was published in *P. Liao and E. A. Carter, "Ab initio DFT+U predictions of tensile properties of iron oxides," J. Mater. Chem., 20, 6703 (2010).*

Turning to shear response, we used the renormalization model proposed in our earlier work on chromia to extrapolate atomic scale shear strengths (derived from ab initio DFT+U calculations) to those of macroscopic sample sizes. Like the tensile strengths, the extrapolated macroscopic predictions are consistent with measurements. The shear strengths of FeO and Fe_3O_4 are predicted to be similar, ~ 4.5 MPa, while the shear strength of Fe_2O_3 is predicted to be the largest, ~ 7 MPa, for samples 5 mm thick. The preferred slip systems are predicted to be $\{0001\}\langle 10\bar{1}0\rangle$ for $\alpha\text{-Fe}_2\text{O}_3$ and $\{110\}\langle 1\bar{1}0\rangle$ for both FeO and Fe_3O_4 . These shear strengths are significantly lower than the corresponding tensile strengths, suggesting that these oxide scales are likely to slip before fracturing. This work was published in *P. Liao and E. A. Carter, "Ab initio DFT+U predictions of the shear response of iron oxides," Acta Materialia, 58, 5912 (2010).*

These findings have implications for understanding wear of gun tubes, since shear forces dominate when the projectile move upon gun firing. It suggests that any area where exposed oxide has formed may lose the oxide due to shear followed by mass removal (hence wear). Moreover, our predictions suggest that polycrystalline oxides, especially on the nanoscale, may be the most wear-resistant due to their improved strength.

¹ V. I. Anisimov, F. Aryasetiawan, and A. I. Liechtenstein, "First-principles calculations of the electronic structure and spectra of strongly correlated systems: The LDA+U method," *J. Phys.: Condens. Matter* **9**, 767 (1997); S. L. Dudarev, A. I. Liechtenstein, M. R. Castell, et al., *Phys. Rev. B* **56**, 4900 (1997).

² V. I. Anisimov and O. Gunnarsson, "Density-functional calculation of effective Coulomb interactions in metals," *Phys. Rev. B* **43**, 7570-74 (1991).

³ N.W. Ashcroft and N. D Mermin, *Solid State Physics*, (Saunders, Fort Worth, 1976).